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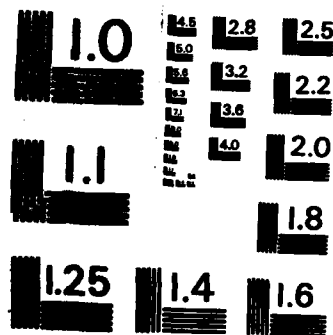
ISOLATION AND CHARACTERIZATION OF AN
ORGANO Gallium-ARSENIC CLUSTER CRYST (U) DUKE UNIV
DURHAM NC DEPT OF CHEMISTRY R L WELLS ET AL 18 JAN 86
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TECHNICAL REPORT * J/DC/TR-01

Isolation and Characterization of an Organogallium-Arsenic
Cluster: Crystal Structure of $[(\text{PhAsH})(\text{R}_2\text{Ga})(\text{PhAs})_6(\text{RGa})_4]$
($\text{R} = \text{Me}_3\text{SiCH}_2$)

by

R. L. Wells, A. P. Purdy, A. T. McPhail, and C. G. Pitt

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Isolation and Characterization of an Organogallium-arsenic
Cluster: Crystal Structure of $[(\text{PhAsH})(\text{R}_2\text{Ga})(\text{PhAs})_6(\text{RGa})_4]$
($\text{R} = \text{Me}_3\text{SiCH}_2$)

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Colin G. Pitt*

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$[(\text{PhAsH})(\text{R}_2\text{Ga})(\text{PhAs})_6(\text{RGa})_4]$ ($\text{R} = \text{Me}_3\text{SiCH}_2$) has been isolated as a product
of the reaction of PhAsH_2 with $(\text{Me}_3\text{SiCH}_2)_3\text{Ga}$ and determined by x-ray
crystallographic analysis to be a cluster containing an As_7Ga_5 core.

As part of our studies of synthetic methods and the identification of
substituents which will permit the isolation of monomeric and oligomeric
gallium-arsenic compounds, we investigated the reaction of PhAsH_2 with
 $(\text{Me}_3\text{SiCH}_2)_3\text{Ga}$. Primarily, it was of interest to ascertain if steric bulk
would permit the isolation of compounds of the type $(\text{PhAsGaCH}_2\text{SiMe}_3)_n$ ($n =$
1-4) and suppress formation of polymers similar to the nonvolatile polymeric
material reported to be the primary product of the reaction of PhAsH_2 with
 Me_3Ga . Although no evidence for any of the desired compounds was obtained
when PhAsH_2 was allowed to react with $(\text{Me}_3\text{SiCH}_2)_3\text{Ga}$, the novel cluster
 $[(\text{PhAsH})(\text{R}_2\text{Ga})(\text{PhAs})_6(\text{RGa})_4]$ ($\text{R} = \text{Me}_3\text{SiCH}_2$), (1), containing an As_7Ga_5 core

was eventually isolated from the complex mixture of products formed. In addition, the known compound $(\text{PhAs})_6^3$ was isolated.

A mixture of PhAsH_2 and $(\text{Me}_3\text{SiCH}_2)_3\text{Ga}$ (1.0 : 0.95 mol ratio), warmed in stages to 50°C , reacted smoothly, as evidenced by the formation of Me_4Si and a non-condensable gas (presumably H_2). The pentane extract of the nonvolatile products afforded a viscous liquid-solid mixture. Crystals of (1)[†] precipitated slowly from the ligroin soluble fraction of this mixture. Crystallization of the pentane-insoluble products from benzene and then tetrahydrofuran afforded $(\text{PhAs})_6^+$.

Crystal Data. $\text{C}_{66}\text{H}_{102}\text{As}_7\text{Ga}_5\text{Si}_6$, (1), $M = 1937.12$, Triclinic, space group $\overline{P}1$, $a = 15.398(2)$, $b = 21.755(1)$, $c = 15.155(1)$ Å, $\alpha = 96.43(1)$, $\beta = 114.42(1)$, $\gamma = 100.43(1)^\circ$, $V = 4446.1$ Å³, $Z = 2$, $D_c = 1.447$ g cm⁻³, $\mu(\text{Cu-K}\alpha) = 56.6$ cm⁻¹. The crystal structure was solved by direct methods.⁴ Least-squares refinement of atomic positional and thermal (anisotropic As, Ga, Si; isotropic C) parameters⁵ converged to $R = 0.074$ over 12276 absorption-corrected reflections [$I > 3.0\sigma(I)$] recorded on an Enraf-Nonius CAD-4 diffractometer (Cu-K α radiation, incident-beam graphite monochromator; ω - 2θ scans, $\theta_{\text{max}} = 67^\circ$). The final difference Fourier map shows residual electron density around the center of symmetry due to partial occupancy by hydrocarbons from the ligroin used to crystallize (1). The calculated density, given above, omits the unknown extent of solvent present.

The structure of one enantiomer and its Ga-As core are presented in Figure 1. The Ga-As core of the cluster may be viewed in several different ways, one of which is to consider it as being comprised of an eight-membered

As(2)-Ga(5)-As(3)-Ga(7)-As(9)-Ga(10)-As(11)-Ga(12) ring in a distorted crown form with three axial Ga sites linked on one side of the ring by an As(1)-As(8) unit, while on the opposite side of the ring three axial As sites are bridged by an As(4)-Ga(6) moiety. Alternatively, it may be viewed as being comprised of two nonplanar five-membered rings [(As(4)-As(2)-Ga(12)-As(11)-Ga(6) and As(8)-As(1)-Ga(7)-As(3)-Ga(5)] linked by As(1)-Ga(12), As(2)-Ga(5), and As(3)-Ga(6) bonds, and bridged by an As(9)-Ga(10) unit. The single hydrogen atom bonded directly to an arsenic atom could not be located unequivocally in a difference Fourier synthesis, but of the three possible sites, viz. As(4), As(8), or As(9), the latter seems most likely since this atom is adjacent to the unique gallium atom bearing two Me_3SiCH_2 groups, i.e. Ga(10). Support for this assignment derives from the fact that the mean bond angles at As(4) and As(8) are 97.1 and 97.8° , respectively; whereas at As(9) the mean is 113.3° . Ga-As bond lengths in (1) range from $2.450(1)$ to $2.553(1)$ Å, with the mean at 2.503 Å being intermediate between the means of 2.524 Å in the centrosymmetric dimer $[(\text{Me}_3\text{SiCH}_2)_2\text{AsGaPh}_2]_2$ ⁵ and 2.492 Å in monomeric $(\text{Mes}_2\text{As})_3\text{Ga}$ ⁶ which contains a trigonal planar gallium atom.

To the best of our knowledge, compound (1) is the first cluster compound containing a core of gallium and arsenic atoms to be isolated and characterized. Although it is not possible to account precisely for its formation, we have previously observed that hydrogen and diarsines are by-products of the reactions of hindered gallanes, e.g. $(\text{Me}_3\text{SiCH}_2)_3\text{Ga}$, and secondary arsines.⁷ Thus, it is not too surprising to find that a compound

such as $(\text{PhAs})_6$ is produced in the reaction of PhAsH_2 with $(\text{Me}_3\text{SiCH}_2)_3\text{Ga}$, and that (1) contains As-As bonds as well as Ga-As bonds

We thank the Office of Naval Research for financial support.

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- 7 R. L. Wells, A. P. Purdy, and C. G. Pitt, unpublished results.

Footnotes

+ Compound (1) mp 153 °C, dec. Anal. Calcd for $C_{66}H_{102}As_7Ga_5Si_6$: C, 40.92; H, 5.31. Found: C, 41.27; H, 5.59. 1H nmr (ppm) (250MHz), C_7D_8 : complex -0.6 to 0.6 (Me_3SiCH_2), and 6.7 to 8.4 (Ph); five peaks 3.2 to 4.1 (AsH).

† Identified by comparison of recorded x-ray diffraction data with those given in ref. 3.

§ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

Figure 1. Structure of a. compound (1), and
b. the Ga-As core of compound (1)

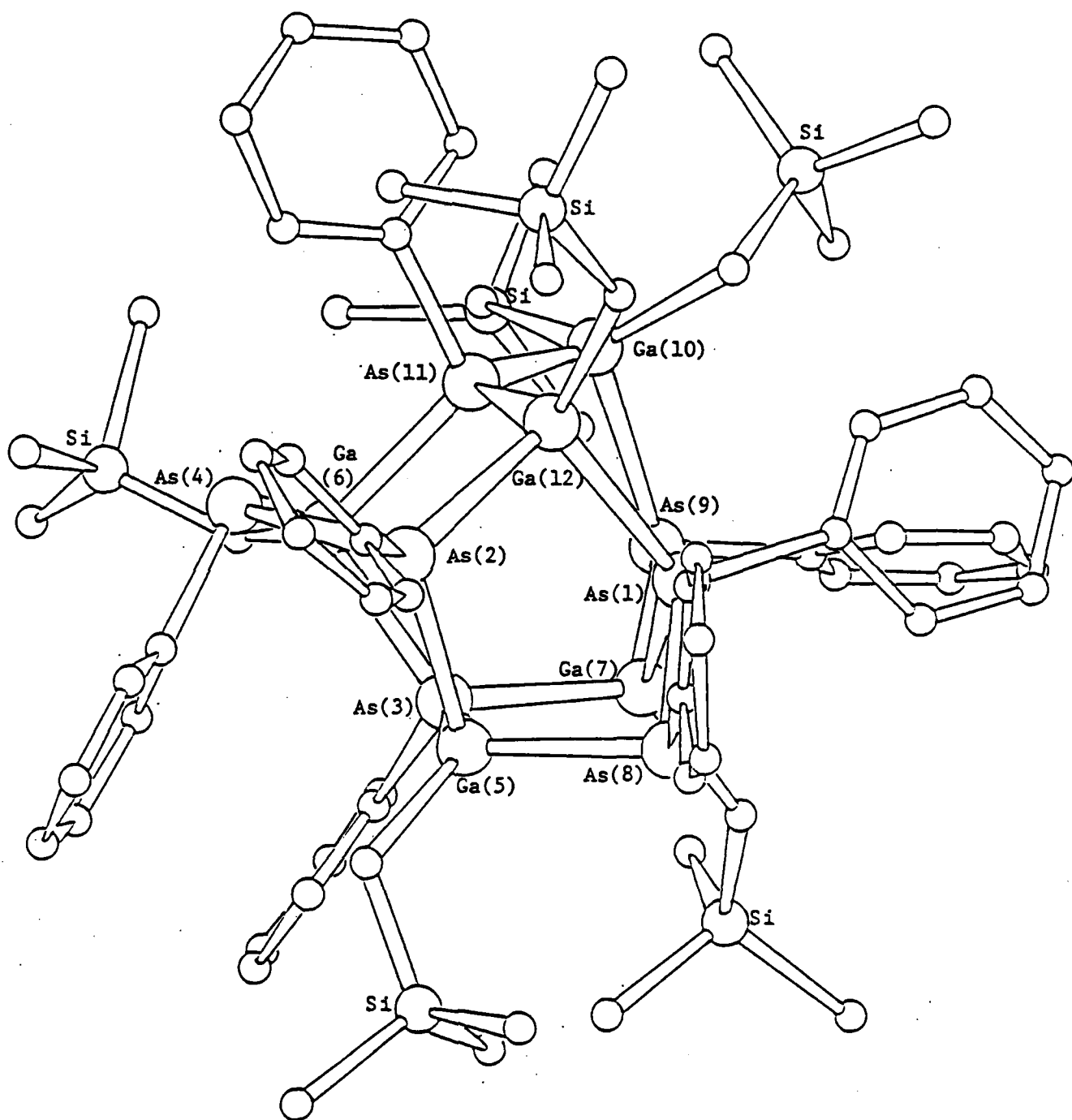
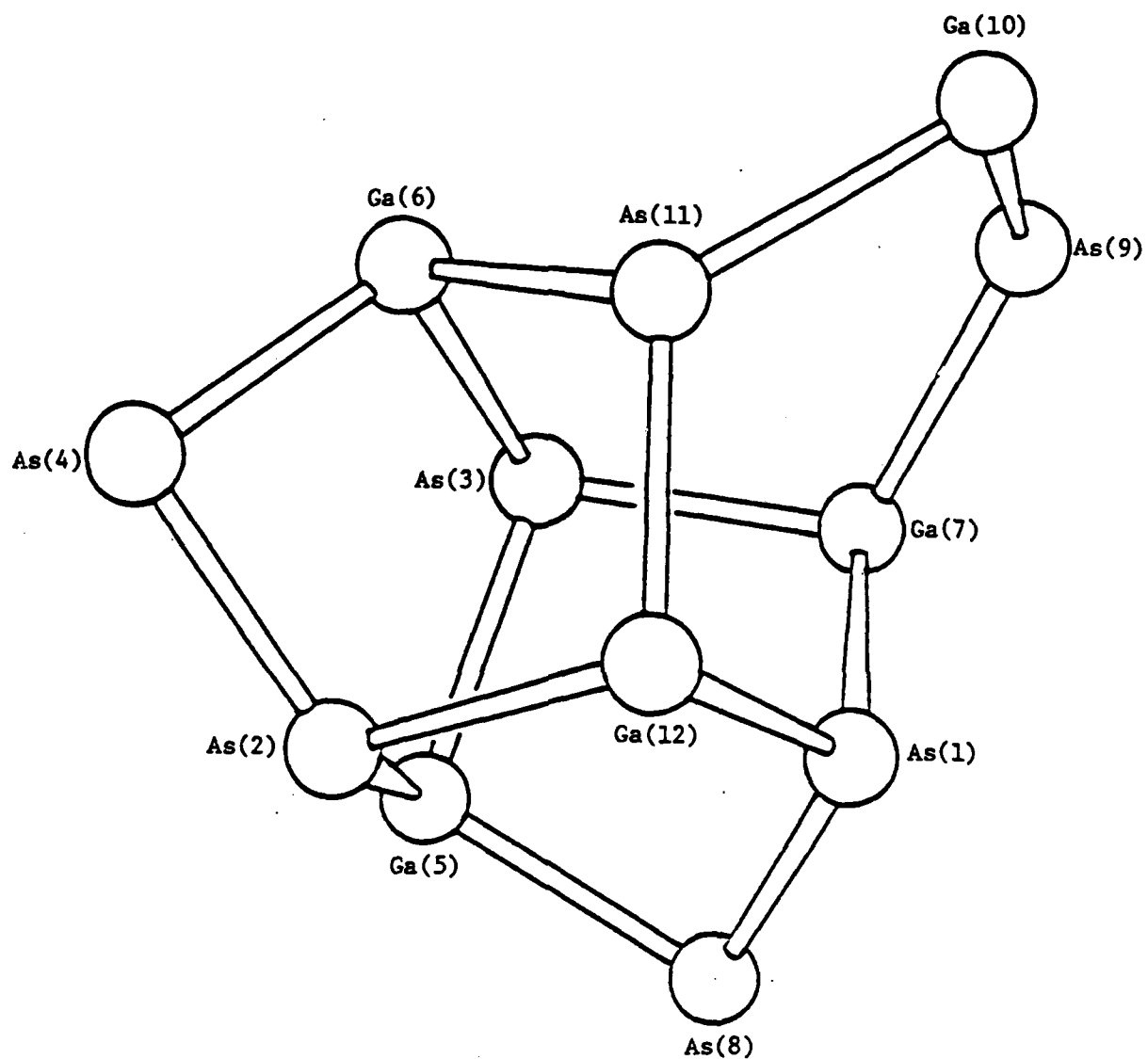


Fig. 1a.



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